Theoretical calibration of a new paleothermometer based on ^{13}C-^{18}O clumping in carbonate minerals

Edwin A. Schauble
Department of Earth and Space Sciences
University of California, Los Angeles
Los Angeles, CA 90095-1567
USA
schauble@ess.ucla.edu

John M. Eiler
Division of Geological and Planetary Sciences
California Institute of Technology
USA

Prosenjit Ghosh
Division of Geological and Planetary Sciences
California Institute of Technology
USA

Recent measurements of CO_2 molecules containing both ^{13}C and ^{18}O (i.e., $^{13}C^{18}O^{16}O$) at natural, ppm-level abundances[1] have shown that CO_2 formed at low temperatures contains a small, temperature-dependent $^{13}C^{18}O^{16}O$ excess (~1‰ at 298 K). This has made it possible to track sources and sinks of atmospheric gases from a new perspective. Carbonate minerals like calcite ($CaCO_3$) are known to retain isotopic signatures over geological timescales, suggesting that measurements of multiply-substituted, or "clumped" ^{13}C-^{18}O-bearing carbonate groups could improve our understanding of ancient and extraterrestrial climates. ^{13}C-^{18}O clumping is an internal property of each phase, so temperature information can be obtained even when the isotopic composition of the fluid phase from which a sample precipitated is not known. This study estimates the abundances of ^{13}C-^{18}O-substituted CO_3^{2-} groups in carbonates using *ab initio* thermodynamic modeling, and compares the results to initial measurements of laboratory and natural samples.

Our calculations indicate that carbonate minerals equilibrated at modern earth-surface temperatures will have a slight overabundance of CO_3^{2-} groups containing both ^{13}C and ^{18}O (i.e., $^{13}C\,^{18}O^{16}O_2^{2-}$) relative to what would be expected if carbon and oxygen isotopes were distributed randomly in the crystal lattice. Calcite, dolomite and aragonite will have 0.4‰-0.5‰ excesses of $^{13}C^{18}O^{16}O_2^{2-}$ at 298 K. Clumping is less pronounced at higher temperatures, disappearing above 1000 K. Experimental results from modern corals and carbonates partially re-equilibrated at higher temperatures suggest an 0.7‰ excess of $^{13}C^{18}O^{16}O_2^{2-}$ at ~300 K, with a slightly stronger temperature sensitivity than predicted.

[1]Eiler et al. 2004, GCA 68:4767.